



# Pd-doped $\text{LaCoO}_3$ regenerative catalyst for automotive emissions control

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## ABSTRACT

The effect of partial substitution of Co by Pd in  $\text{LaCoO}_3$  perovskite structure (i.e.,  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$ ) and the reductive diffusion of Pd from the bulk of perovskite to its surface, thus forming Pd nanoparticles, on CO and  $\text{C}_3\text{H}_8$  oxidation present in air (simulated exhaust gas) are reported. X-ray powder diffraction (XRD) analyses confirm the perovskite structure for the catalysts. Scanning electron microscopy (SEM) and BET surface area measurements show that partial substitution of Co by Pd decreases the crystallite size of the perovskite and therefore increases its surface area.  $\text{H}_2$ -temperature programmed reduction (TPR) experiments reveal that Pd reduces at  $135^\circ\text{C}$  and facilitates the reduction of Co in the perovskite structure. By partial reduction of the Pd containing catalyst at  $180^\circ\text{C}$  for 30 min, the complete oxidation temperatures of CO and  $\text{C}_3\text{H}_8$  decrease by about 70 and  $50^\circ\text{C}$ , respectively.

The reduction duration of the Pd containing catalyst strongly affects the  $T_{50}$  and  $T_{90}$  temperatures (temperatures at which 50 and 90% conversion occurs, respectively) and has an optimum, where it decreases by increasing the reduction temperature of the catalyst.

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## 1. Introduction

One of the main sources of air pollution in large cities is automotive exhaust gas emissions. Therefore, catalytic converters have been applied for exhaust gas treatment since the 1970s. Conventional three-way automotive exhaust catalysts contain precious metals (Pt, Pd and Rh) for treatment of pollutants such as CO, unburned hydrocarbons and  $\text{NO}_x$  [1]. One of the reasons of deterioration of these catalysts is considered to be due to the decrease in active surface area of precious metals caused by grain growth in high-temperature redox (reduction–oxidation) fluctuations of the exhaust gas. To compensate for this deterioration, conventional catalysts are loaded with excess amounts of precious metals [2].

Due to high prices and limited sources of precious metals, attention has been given to search for an alternative catalytic component to reduce the use or even replace the precious metals. Among the substitute catalysts, perovskite type mixed oxides ( $\text{ABO}_3$ ) have shown promising results. The catalytic properties of perovskites for oxidation of pollutants depend on several factors including the nature of B site cations. For oxidation of CO and hydrocarbons,  $\text{LaCoO}_3$  is known as one of the most active perovskites [3].

Incorporation of small amounts of precious metals into a perovskite structure can prevent their sintering, reduce losses due

to volatilization at high operating temperatures, and avoid reactions with the support that lead to catalyst deactivation [4–6]. Recent attention has been concentrated on the use of palladium-based catalyst for TWC (three-way catalyst) formulation. Pd is well known to have a good resistance to thermal sintering, lower price than Pt and Rh and also have a good activity for oxidation of CO and hydrocarbons [7–10].

The modern gasoline engine has adopted a feedback control system that uses an oxygen sensor for three-way catalysts to function in optimum conditions. Therefore, the environment of automotive exhaust gas fluctuates between oxidative and reductive atmospheres through the operation of catalytic converters. A regenerative catalyst is a catalyst which keeps a high activity through these redox fluctuations by adapting its structure to the environment. This adaptation is a reversible response to the conditions of the atmosphere to which the catalyst is exposed. Due to the regenerative function, the Pd containing perovskites, e.g.  $\text{LaFe}_{0.95}\text{Pd}_{0.05}\text{O}_3$ , maintain their high activity in the course of their use as the catalytic converter catalysts. It is suggested that in oxide form, Pd may diffuse into the perovskite lattice and replace the B site cation. In reducing atmospheres, Pd segregates out and disperses as metallic nanoparticles on the surface of the perovskites. Transfer of the Pd between the bulk and the surface occurs in response to the redox conditions of the environment [11–21]. It should be mentioned that  $\text{LaFe}_{0.95}\text{Pd}_{0.05}\text{O}_3$  perovskite has been used industrially as a three-way catalyst for gasoline automotive emission control since October 2002 [19].

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The aim of this work is to study the regenerative function of a Pd containing  $\text{LaCoO}_3$  (i.e.,  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$ ) and the effect of partial reduction on enhancing its catalytic activity as a catalyst for abatement of the automotive exhaust gas pollutants. Although the present catalyst investigated may not have practical interest for the TWC application, due to the presence of Co which is reported to be carcinogenic; however, it was used as a model system to study the regenerative behavior of Pd-based perovskites, and in particular how the reduction conditions (temperature, time) affect the catalyst activity behavior.

## 2. Experimental

### 2.1. Catalyst preparation

$\text{LaCoO}_3$  and  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$ , containing 2.1 wt% Pd, catalysts were prepared via citrate method [22]. In the course of synthesis, solutions containing stoichiometric amounts of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (all high purity salts from Merck) and also citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ , Merck) were prepared. The molar ratio of citric acid to total nitrate ions was fixed at unity. Solutions were heated in two steps, first at 80 °C overnight followed by heating at 150 °C overnight to yield brown spongy cakes which were grounded and calcined at 700 °C in air for 5 h.

### 2.2. Pre-reduction

In order to study the effect of reduction on regeneration of  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  catalyst activity, samples were partially reduced by 3.0%  $\text{H}_2$  in He with flow rate of 100  $\text{cm}^3$  STP/min prior to each catalytic activity test. The pre-reduction temperature was set in a salt bath by a temperature controller. Effects of various pre-reduction durations (from 0 to 60 min) on catalytic activity were investigated at two different reduction temperatures of 180 and 250 °C. After reduction, the catalyst bed was purged by He while cooling down to room temperature and then passivated by 0.5%  $\text{O}_2$  in Ar for 15 min. The catalytic activity tests were then carried out.

### 2.3. Catalyst characterization

The crystal structures of the catalysts were determined by X-ray powder diffraction (XRD) with a Bruker AXS D8 Advanced diffractometer using  $\text{Cu K}\alpha$  radiation. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were done by a Philips XL30 instrument to investigate the crystal size and morphology as well as the elemental composition of the catalysts.

BET and  $\text{H}_2$ -temperature programmed reduction (TPR) tests were carried out using a Quantachrome CHEMBET-3000 apparatus. BET surface areas were measured at the liquid nitrogen temperature by  $\text{N}_2$  adsorption, using the single point method. The TPR experiments were performed on 0.020 g of perovskite samples by 10  $\text{cm}^3$  STP/min of 7.0%  $\text{H}_2$  in Ar. Temperature was raised from 50 to 800 °C with a heating rate of 10 °C/min.

### 2.4. Catalytic activity measurement

Mixture of 6.0% CO and 0.2%  $\text{C}_3\text{H}_8$ , as a hydrocarbon (HC) model compound, in Ar was used as exhaust gas pollutants. Flow rates of this gas mixture and air were set by mass flow controllers in order to obtain a synthetic exhaust gas with total flow rate of 50  $\text{cm}^3$  STP/min and SN = 1.1, where SN is stoichiometric number with the definition of  $\text{SN} = 2[\text{O}_2]/([\text{CO}] + 10[\text{C}_3\text{H}_8])$ .

Oxidation of the synthetic exhaust gas pollutants was studied in a fixed bed microreactor at atmospheric pressure. All perovskite samples were pelleted, crushed and sieved to particle size of 0.125–0.297 mm (50–120 mesh sized). 0.250 g of each perovskite,

supported on a small amount of ceramic wool, was used for measuring oxidation activities of the catalysts. The reactor temperature was raised from 100 to 500 °C in a tubular furnace by a temperature controller. A thermocouple, placed inside the catalyst bed, was used for both monitoring and controlling the temperature of the reactor. Concentration of the effluents was analyzed by Shimadzu GC-8A gas chromatograph equipped with a methanizer and an FID. Also a set of valves allowed bypassing the reactor feed directly into the gas chromatograph, which provided a direct measurement of the pollutants concentrations in the feed.

For conversion measurements versus temperature, a start was made at the desired temperature and after steady state was achieved concentration of the effluents was analyzed. The temperature was then increased to the next level and again after steady state was realized, analysis of the reaction products was performed. This procedure was repeated for the whole temperature range, i.e. 100–500 °C, used in this investigation.

## 3. Results and discussion

### 3.1. Catalyst characterization results

XRD patterns of fresh  $\text{LaCoO}_3$  and  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  catalysts, calcined at 700 °C for 5 h, are given in Fig. 1. The patterns show only the perovskite structure for both  $\text{LaCoO}_3$  and  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$ . No peak characterizing Pd or palladium oxide is observed in the  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  spectrum. The XRD pattern of pre-reduced  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  at 180 °C for 30 min (not shown here) also shows the same perovskite pattern. The following TPR results (see Fig. 3) show that Pd can be reduced at 180 °C. However, due to its low concentration (2.1 wt%), Pd peaks do not appear in the XRD pattern of Pd containing perovskite.

BET surface areas of the prepared  $\text{LaCoO}_3$  and  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  were 4.9 and 6.9  $\text{m}^2/\text{g}$ , respectively. About 40% increase in the surface area of  $\text{LaCoO}_3$  is observed after Co is partially substituted by Pd. Increases in the surface area of  $\text{LaFeO}_3$  perovskite by Pd addition have been reported by other researchers [17,23].

Fig. 2 presents the SEM micrographs of the catalysts. Surface morphology of  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  shows that the perovskite particles are agglomerated and have smaller size compared to  $\text{LaCoO}_3$ . This result is in agreement with the increase in BET surface area for  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$ . EDS analysis confirms the presence of approximately 2 wt% Pd in the structure of the prepared  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  catalyst.

Fig. 3 presents the TPR profiles of the fresh  $\text{LaCoO}_3$ ,  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  and pre-reduced  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  at 180 °C for

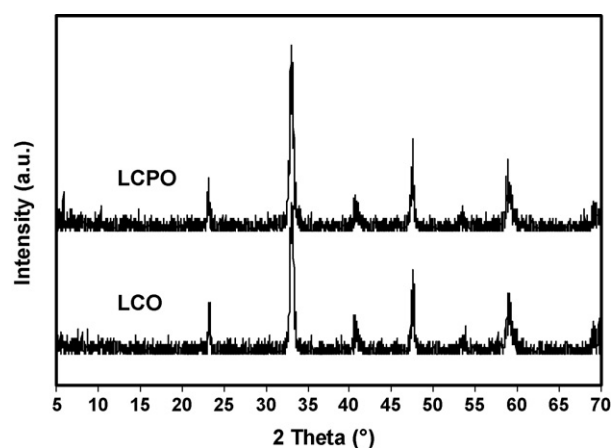
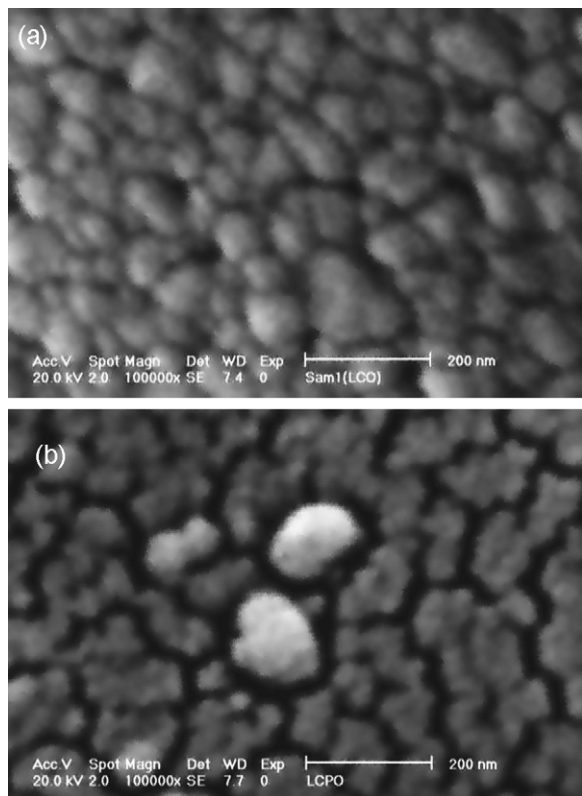


Fig. 1. XRD patterns of fresh  $\text{LaCoO}_3$  (LCO) and  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  (LCPO) prepared by citrate method, calcined at 700 °C for 5 h.

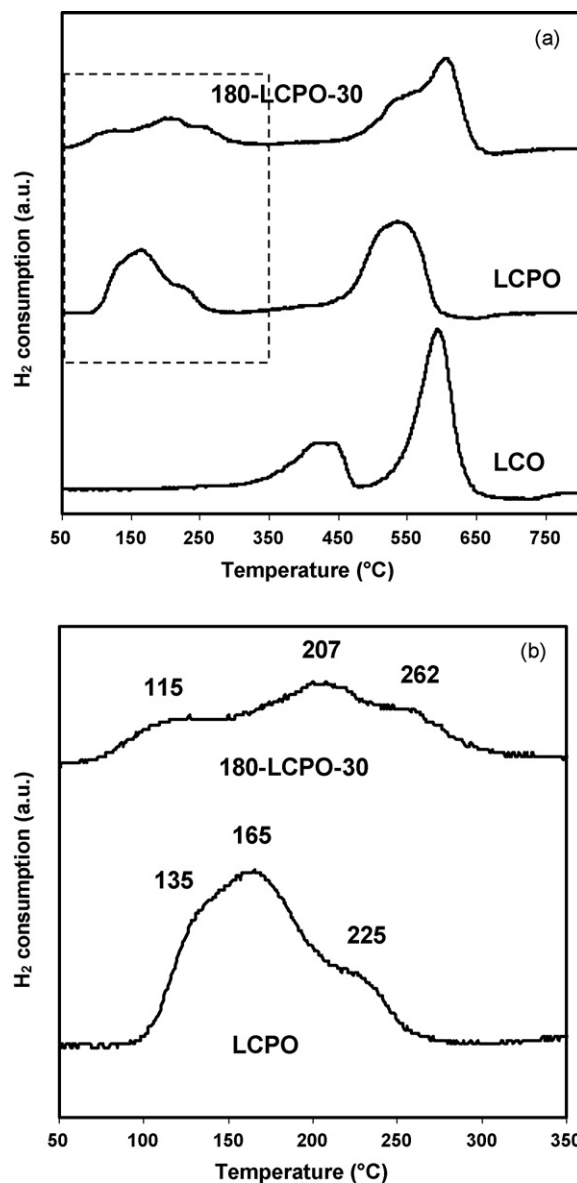


**Fig. 2.** SEM micrographs of the catalysts prepared by citrate method, calcined at 700 °C for 5 h: (a) LaCoO<sub>3</sub> and (b) LaCo<sub>0.95</sub>Pd<sub>0.05</sub>O<sub>3</sub>.

30 min. The TPR profile of LaCoO<sub>3</sub> shows two successive reduction peaks, one in the range of 340–480 °C and the other at 500–670 °C ( $T_{\max} = 600$  °C). These successive reduction steps are observed for all LaCoO<sub>3</sub> perovskites, as reported by several authors [24,25]. The first reduction peak is described in the literature as the reduction of Co<sup>3+</sup> into Co<sup>2+</sup> and the second one is attributed to the reduction of Co<sup>2+</sup> to Co<sup>0</sup>.

The TPR profile of LaCo<sub>0.95</sub>Pd<sub>0.05</sub>O<sub>3</sub> catalyst shows that the high-temperature reduction peak of Co in LaCoO<sub>3</sub> shifts to lower temperatures by 60 °C ( $T_{\max} = 540$  °C). The similar result was observed for LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> when 2.6 wt% Pd was introduced into its lattice (i.e., LaFe<sub>0.77</sub>Co<sub>0.17</sub>Pd<sub>0.06</sub>O<sub>3</sub>) [26]. Moreover, the same observation has been reported for LaFe<sub>0.97</sub>Pd<sub>0.03</sub>O<sub>3</sub> compared to LaFeO<sub>3</sub> [23]. On the other hand, three overlapping low-temperature peaks in Fig. 3 can be recognized at 135, 165 and 225 °C. It should be mentioned that the TPR results were reproducible. It was also ensured that the heating rate in the course of TPR experiments was linear. For 0.5 wt% Pd/LaCoO<sub>3</sub>, Giraudon et al. [27] have reported that the first low-temperature small peak corresponds to the reduction of oxide form of Pd into Pd<sup>0</sup> whereas other ones are assigned to the reduction of Co. As a result it is suggested that Pd facilitates the reduction of Co and therefore increases the reducibility of the catalyst. It is reported that the role of Pd can be attributed to hydrogen dissociation at the surface of the Pd<sup>0</sup> particles, already formed at low temperatures, and the successive spillover of dissociated hydrogen atoms which facilitates the reduction of support [28].

Pre-reduced LaCo<sub>0.95</sub>Pd<sub>0.05</sub>O<sub>3</sub> at 180 °C for 30 min was also subjected to TPR tests (see Fig. 3). Number of the peaks and the reduction temperatures are changed for the catalyst which is partially reduced. Two overlapping peaks are observed with the maxima at 540 and 600 °C which are corresponding to the high-temperature peaks in the profiles of LaCo<sub>0.95</sub>Pd<sub>0.05</sub>O<sub>3</sub> and LaCoO<sub>3</sub>,



**Fig. 3.** TPR profiles of fresh LaCoO<sub>3</sub> (LCO), LaCo<sub>0.95</sub>Pd<sub>0.05</sub>O<sub>3</sub> (LCPO) and pre-reduced LaCo<sub>0.95</sub>Pd<sub>0.05</sub>O<sub>3</sub> at 180 °C for 30 min (180-LCPO-30) by 10 cm<sup>3</sup> STP/min of 7% H<sub>2</sub> in Ar, 10 °C/min from 50 to 800 °C: (a) the whole TPR patterns and (b) zoomed low-temperature peaks.

respectively. By considering the low-temperature peaks more carefully (see Fig. 3b) it will be noticed that the reduction of Pd occurs at 115 °C, 20 °C lower than that in LaCo<sub>0.95</sub>Pd<sub>0.05</sub>O<sub>3</sub> and in contrast, an upward shift to 207 and 262 °C is observed for Co low-temperature peaks. It seems that the reduction of Co in this profile tends to shift towards that of Co in LaCoO<sub>3</sub> perovskite.

It has been shown that in oxide form, Pd occupies the B site of LaFe<sub>1-x-y</sub>Co<sub>x</sub>Pd<sub>y</sub>O<sub>3</sub> and LaFe<sub>1-x</sub>Pd<sub>x</sub>O<sub>3</sub> crystal lattice. By different techniques including X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine-structure (EXAFS), it is proved that in reducing atmospheres, Pd segregates out of the lattice of these perovskites and disperses in the form of very fine metallic nanoparticles (1–3 nm) on the surface of the catalysts [11–21]. Zhou et al. [26] have shown that Pd nanoparticles impregnated on the perovskite support reduce at lower temperatures compared to Pd which is partially substituted in the perovskite lattice. Considering the above conclusions and the lower Pd reduction temperature for the pre-reduced catalyst compared to the fresh one in our TPR results, it is

suggested that by pre-reduction treatment, a fraction of Pd in the  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  lattice segregates on its surface. As the Pd content of  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  is too low, the Pd segregation explains why the TPR profile of Pd containing catalyst shifts towards that of the Pd-free  $\text{LaCoO}_3$  after pre-reduction; the reduction peak at  $540^\circ\text{C}$  in the profile of pre-reduced catalyst can be attributed to reduction of Co species which are still highly interacting with residual Pd atoms in the perovskite lattice while the peak at  $600^\circ\text{C}$  can be related to reduction of Co which has less interaction with Pd, due to Pd segregation out of the perovskite lattice. This hypothesis is further confirmed by catalytic activity results.

### 3.2. Catalytic activity results

Fig. 4 presents the catalytic activity results of fresh  $\text{LaCoO}_3$  and  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  catalysts together with the pre-reduced ones for CO and  $\text{C}_3\text{H}_8$  oxidation. All of the catalysts show S-shape profiles for conversion of the polluting gases versus temperature.  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$ , in which Co of  $\text{LaCoO}_3$  perovskite is partially substituted by Pd, shows even lower activity for CO oxidation as compared to the Pd-free catalyst. However, higher activity is obtained for both CO and HC oxidation over the  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  catalyst, pre-reduced at  $180^\circ\text{C}$  for 30 min. In this case, the light-off temperature (temperature at which 50% conversion occurs, i.e.,  $T_{50}$ ) is reduced by 43 and  $49^\circ\text{C}$  for CO and HC oxidation, respectively. Pre-reduced  $\text{LaCoO}_3$  at  $180^\circ\text{C}$  for 30 min was also subjected to the catalytic activity test for comparison. As it can be observed in Fig. 4, partial reduction at this temperature has just a

minor effect on enhancing the catalytic activity of Pd-free  $\text{LaCoO}_3$  as compared to  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  catalyst.

As it was mentioned earlier in Section 3.1, in reducing atmospheres Pd segregates out of the perovskite lattice and disperses as metallic nanoparticles on the surface of the perovskite. On the other hand, it is shown that for the same Pd content, the catalytic activity of Pd/ $\text{LaFe}_{0.8}\text{Co}_{0.2}\text{O}_3$  is higher than that of  $\text{LaFe}_{0.77}\text{Co}_{0.17}\text{Pd}_{0.06}\text{O}_3$  for elimination of automotive pollutants; since Pd nanoparticles are exposed to the reactants in the former catalyst [26]. Considering the above conclusions and the TPR results, the high catalytic activity of pre-reduced  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  can be attributed to fine Pd nanoparticles dispersed on the surface of  $\text{LaCoO}_3$  after this catalyst is exposed to the reducing atmosphere.

In order to investigate the effect of pre-reduction duration on enhancing the catalytic activity of  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  catalyst, the pre-reduction time was varied between 0 and 60 min at  $180^\circ\text{C}$  prior to each catalytic activity test. Temperatures of 50 and 90% conversion ( $T_{50}$  and  $T_{90}$ ) of CO and HC are extracted from the catalytic activity test results. Fig. 5 shows the dependence of  $T_{50}$  and  $T_{90}$  of pollutants conversion on catalyst pre-reduction duration at  $180^\circ\text{C}$ . To demonstrate the effect of Pd addition to  $\text{LaCoO}_3$  and its pre-reduction, dashed lines are also included to show the fresh  $\text{LaCoO}_3$  levels of  $T_{50}$  and  $T_{90}$ . The catalytic activity of  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  significantly enhances by the pre-reduction at  $180^\circ\text{C}$ , the duration of which has an optimum value of 30 min for both CO and HC conversion. By pre-reduction, the  $T_{90}$ 's of CO and HC reduce, respectively, by 56 and  $41^\circ\text{C}$  at the optimum period of 30 min reduction at  $180^\circ\text{C}$ .

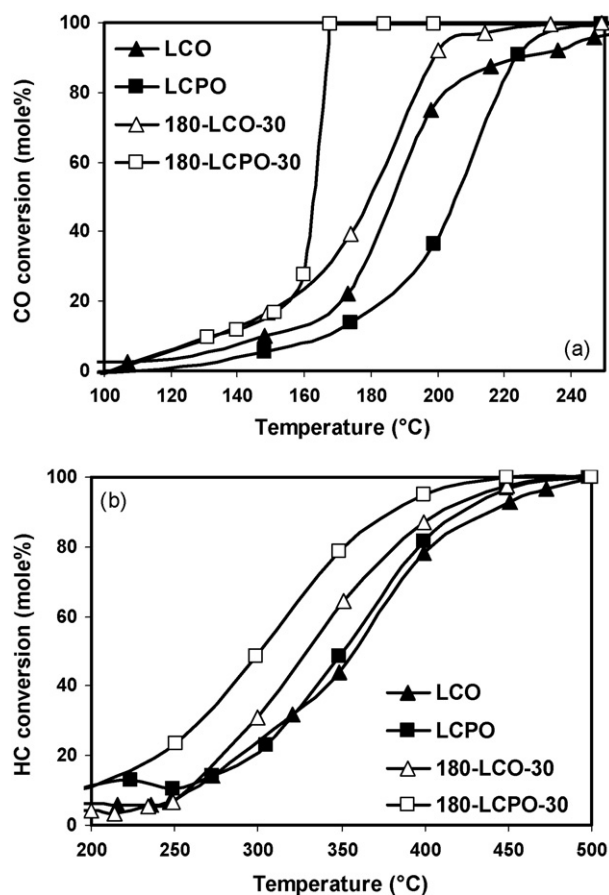


Fig. 4. Catalytic activity of fresh  $\text{LaCoO}_3$  (LCO), fresh  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  (LCPO), pre-reduced  $\text{LaCoO}_3$  at  $180^\circ\text{C}$  for 30 min (180-LCO-30) and pre-reduced  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  at  $180^\circ\text{C}$  for 30 min (180-LCPO-30) for (a) CO and (b) HC oxidation. Amount of catalyst = 0.250 g, total flow =  $50\text{ cm}^3\text{ STP/min}$  and  $\text{SN} = 1.1$ .

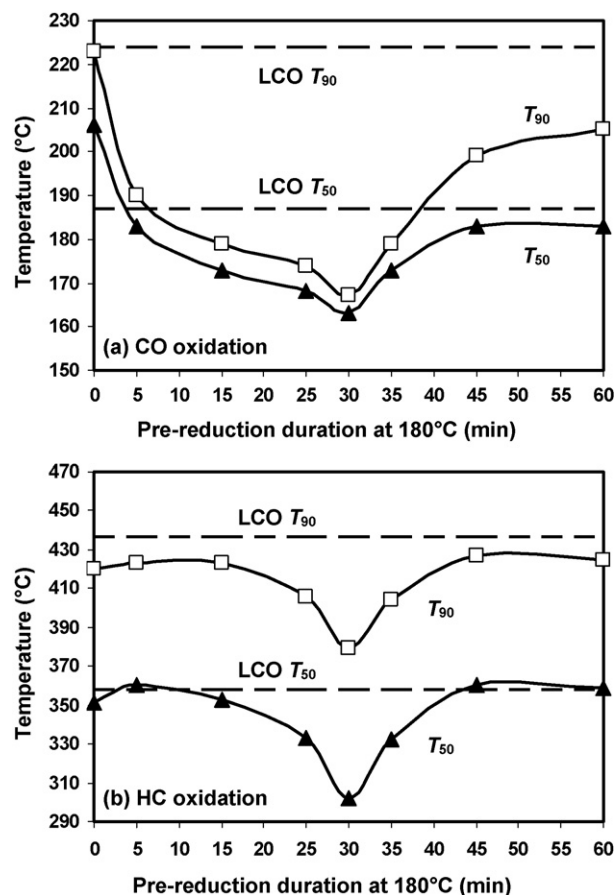


Fig. 5. Dependence of the temperature of 50% conversion ( $T_{50}$ , ▲) and 90% conversion ( $T_{90}$ , □) of (a) CO and (b) HC on  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  catalyst reduction duration at  $180^\circ\text{C}$ . Dashed lines are  $T_{50}$  and  $T_{90}$  for the fresh  $\text{LaCoO}_3$ .



Here we may consider two different phenomena which are taking place at the same time in the course of the catalyst pre-reduction: (1) reducing of Pd from oxide form to metallic nanoparticles while it is segregating out of the perovskite lattice to the catalyst surface and (2) sintering of the nanoparticles at the catalyst surface. It may be assumed that before 30 min of reduction at 180 °C the first phenomenon is the main cause of catalytic activity improvement. Beyond 30 min, the second phenomenon of sintering prevails and therefore the catalytic activity declines. However, the activity of pre-reduced catalyst for CO oxidation is always higher than that of fresh  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  and  $\text{LaCoO}_3$  for the presence of Pd at the surface of the catalyst and its exposure to the reactants.

The higher pre-reduction temperature of 250 °C was also investigated for the effect of rising the reduction temperature on the  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  catalytic performance. Fig. 6 presents the dependence of  $T_{50}$  and  $T_{90}$  of CO and HC conversion on the catalyst pre-reduction duration at 250 °C. Dashed lines indicate the fresh  $\text{LaCoO}_3$  levels of  $T_{50}$  and  $T_{90}$ . The optimum pre-reduction duration reduces from 30 to 15 min as the reduction temperature increases from 180 to 250 °C. This may be attributed to an increase in both the degree of reduction of Pd species to  $\text{Pd}^0$  nanoparticles and their sintering with temperature. Uenishi et al. [14] have reported that for the same duration and conditions of reduction, the ratio of segregated Pd from the  $\text{LaFe}_{0.95}\text{Pd}_{0.05}\text{O}_3$  lattice increases by the increase in reduction temperature.

In order to investigate the activity deterioration of the pre-reduced catalyst at reaction conditions (SN = 1.1), deactivation test was performed at 165 °C on  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  which was pre-reduced at 180 °C for 30 min (Fig. 7). Fig. 7 presents that the CO

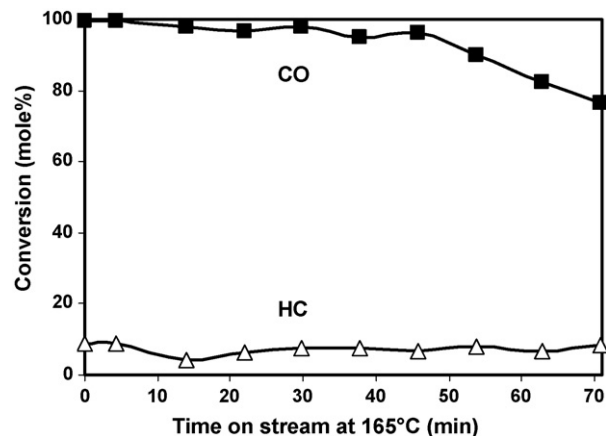


Fig. 7. Deactivation test at 165 °C on pre-reduced  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  at 180 °C for 30 min. Amount of catalyst = 0.250 g, total flow = 50 cm<sup>3</sup> STP/min and SN = 1.1.

conversion at 165 °C slowly declines up to about 45 min, after which a sharp decline in the activity of the catalyst occurs. HC conversion is less than 10% at this temperature and remained almost steady during the experiment. The loss of the catalytic activity for CO oxidation may be ascribed to the oxidation of Pd and its diffusion into the perovskite structure in lean (excess  $\text{O}_2$ ) reaction conditions. This prevents the exposure of the highly active

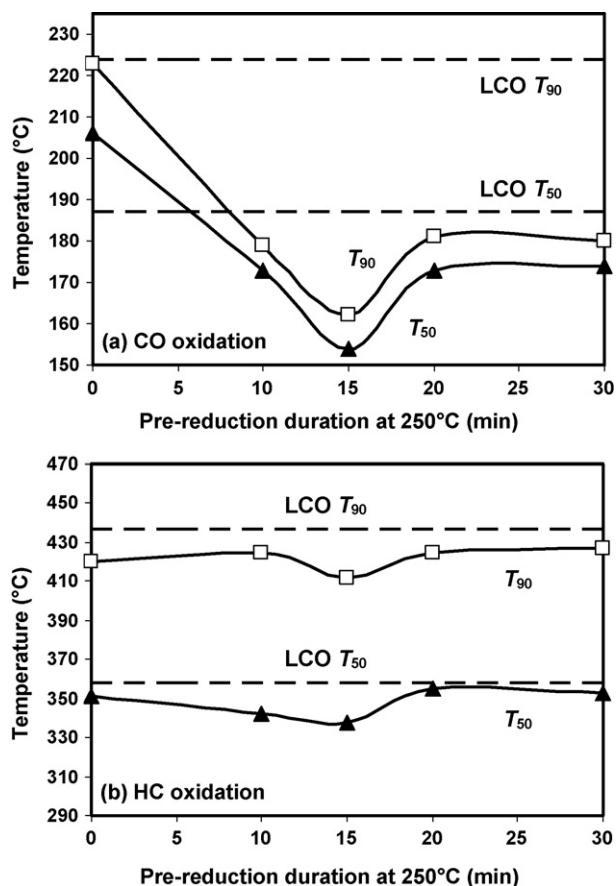


Fig. 6. Dependence of the temperature of 50% conversion ( $T_{50}$ , ▲) and 90% conversion ( $T_{90}$ , □) of (a) CO and (b) HC on  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  catalyst reduction duration at 250 °C. Dashed lines are  $T_{50}$  and  $T_{90}$  for the fresh  $\text{LaCoO}_3$ .

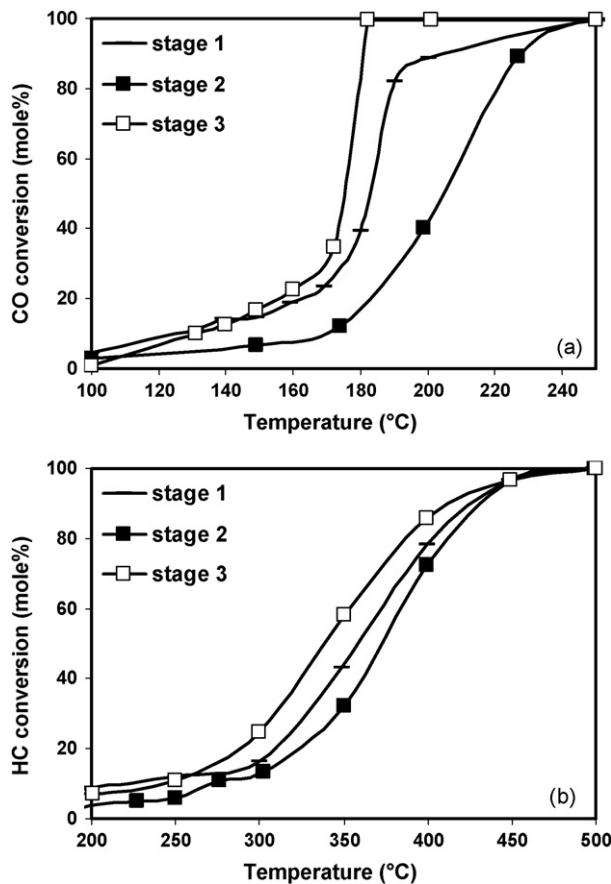
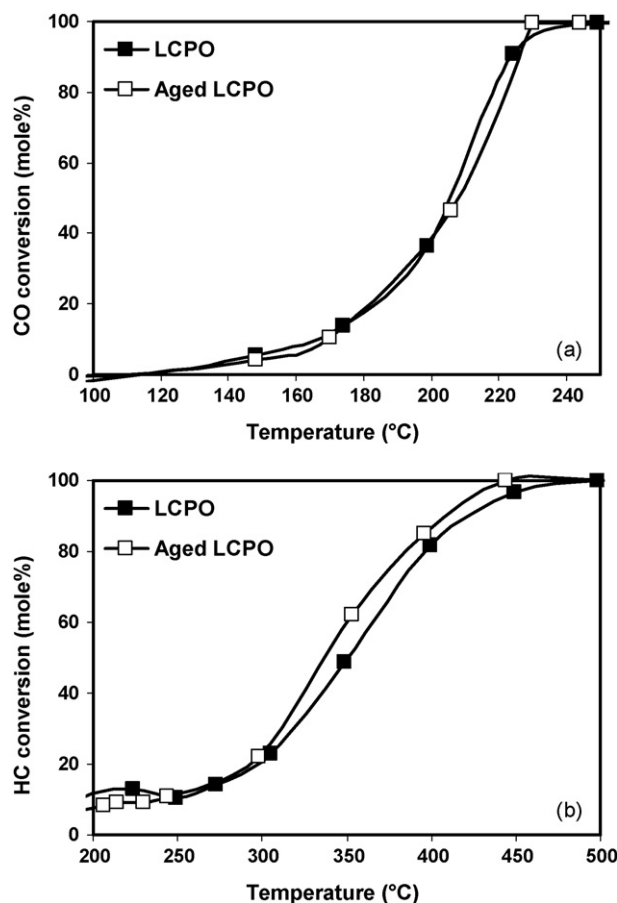


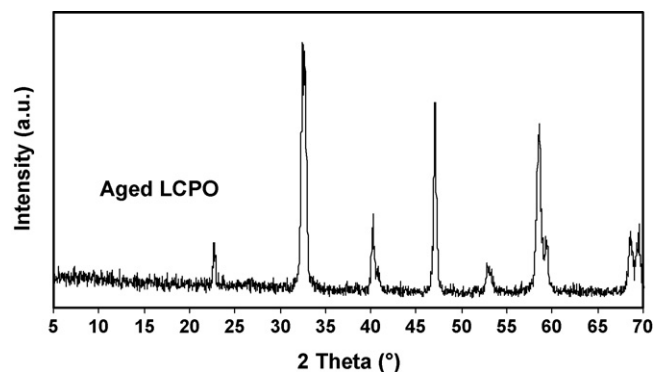
Fig. 8. Effect of successive pre-reduction on the catalytic activity of  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  catalyst for (a) CO and (b) HC oxidation: (stage 1) activity test on pre-reduced  $\text{LaCo}_{0.95}\text{Pd}_{0.05}\text{O}_3$  for 60 min at 180 °C; (stage 2) activity test successively performed on the same sample after cooling down to room temperature, without any pre-treatment and (stage 3) activity test successively performed on the same sample pre-reduced for 30 min at 180 °C. Amount of catalyst = 0.250 g, total flow = 50 cm<sup>3</sup> STP/min and SN = 1.1.



**Fig. 9.** Catalytic activity of fresh LaCo<sub>0.95</sub>Pd<sub>0.05</sub>O<sub>3</sub> (LCPO) and aged LaCo<sub>0.95</sub>Pd<sub>0.05</sub>O<sub>3</sub> at 850 °C for 660 min in reaction conditions (aged LCPO) for (a) CO and (b) HC oxidation. Amount of catalyst = 0.250 g, total flow = 50 cm<sup>3</sup> STP/min and SN = 1.1.

Pd nanoparticles to the CO and HC pollutant gases. Uenishi et al. [14] have proposed that by exposing the pre-reduced Pd containing iron perovskite, on surface of which metallic Pd nanoparticles are dispersed, to an oxidative atmosphere, Pd oxidizes again and diffuses into the perovskite lattice to substitute the B site cation.

As it was mentioned in Section 1, a regenerative catalyst keeps a high activity through redox fluctuations of the exhaust gas by adapting its structure to the reductive and oxidative atmospheres in a reversible manner. In order to investigate the regenerative function of LaCo<sub>0.95</sub>Pd<sub>0.05</sub>O<sub>3</sub>, effect of successive pre-reduction on the catalytic activity performance of this catalyst was tested for CO and HC oxidation in three stages: (1) the catalytic activity test was performed on a sample which was pre-reduced for 60 min at 180 °C; (2) after cooling down the same sample to room temperature, it was tested again without any pre-treatment and (3) finally the same sample was pre-reduced again for 30 min at 180 °C and then subjected to the catalytic activity test for the third time. The catalytic activity test results are presented in Fig. 8. CO light-off temperature of LaCo<sub>0.95</sub>Pd<sub>0.05</sub>O<sub>3</sub> pre-reduced for 60 min at 180 °C is 23 °C lower than that of the fresh catalyst (see Fig. 5a). Comparing the test results of the first and second stages reveals that the catalytic activity of the pre-reduced catalyst decreases after the first catalytic activity test, due to the oxidation of Pd at lean reaction conditions (SN = 1.1). However, pre-reduction of the same catalyst sample at the third stage regenerates the high catalytic activity. As it can be observed in Fig. 8, the catalytic activity of the sample which is pre-reduced for 30 min at the third stage (i.e., for the optimum reduction duration



**Fig. 10.** XRD pattern of aged LaCo<sub>0.95</sub>Pd<sub>0.05</sub>O<sub>3</sub> at 850 °C for 660 min in reaction conditions (aged LCPO).

in Fig. 5), is even higher than that of the catalyst which is pre-reduced for 60 min at the first stage. From this result it can be concluded that even though the excessive reduction of the catalyst to 60 min in the first stage is not favorable for the purposes of catalytic activity, due to sintering of Pd, LaCo<sub>0.95</sub>Pd<sub>0.05</sub>O<sub>3</sub> is able to rearrange its structure in order to maintain a high activity at the third stage and therefore is a regenerative catalyst. By in situ energy-dispersive X-ray absorption fine-structure (EXAFS) analysis, it is reported that the change in structure of Pd in LaFe<sub>1-x</sub>Pd<sub>x</sub>O<sub>3</sub> catalyst is sufficiently fast to respond to the control frequency (1–4 Hz) of an actual gasoline engine [15,18,21].

Finally the catalyst was aged to see if the perovskite structure is stable enough and does not decompose under the reaction conditions. LaCo<sub>0.95</sub>Pd<sub>0.05</sub>O<sub>3</sub> catalyst was aged at 850 °C for 660 min in reaction conditions (total flow = 50 cm<sup>3</sup> STP/min and SN = 1.1) and then subjected to catalytic activity test and XRD analysis. Fig. 9 presents the catalytic activity of the aged catalyst as well as the fresh one for oxidation of CO and HC. In Fig. 9 no activity loss is observed for LaCo<sub>0.95</sub>Pd<sub>0.05</sub>O<sub>3</sub> catalyst after the aging treatment. Moreover, XRD confirms the perovskite structure for the aged catalyst (Fig. 10). Tanaka et al. [13,15,18] have reported that LaFe<sub>0.57</sub>Co<sub>0.38</sub>Pd<sub>0.05</sub>O<sub>3</sub> and LaFe<sub>0.95</sub>Pd<sub>0.05</sub>O<sub>3</sub> catalysts maintained their high TWC activity during and after aging at 900 °C for 100 h by the exhaust of a real engine.

#### 4. Conclusions

The effect of Pd partial substitution in LaCoO<sub>3</sub> perovskite and its regenerative reduction is studied in a simulated exhaust gas for oxidation of CO and C<sub>3</sub>H<sub>8</sub> present in air. Pd addition even lowers the CO oxidation activity. However, partial reduction of the Pd containing catalyst for a proper duration of time significantly enhances the oxidation activity of the catalyst, due to segregation of Pd from the perovskite lattice and its dispersion on the catalyst surface as metallic nanoparticles. Excessive reduction of the Pd containing catalyst for longer durations has an unfavorable effect on the oxidation activity of the catalyst, due probably to sintering of the Pd nanoparticles. The high activity declines in lean reaction conditions after a period of time since Pd re-oxidizes and diffuses back into the perovskite lattice. However, successive reduction regenerates the high activity of the catalyst by re-dispersing Pd nanoparticles on the catalyst surface.

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